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Dual-gate thin-film trasistors for logic and sensors

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Chapter 6

Gas sensing with self-assembled monolayer field-effect transistors

A new sensitive gas sensor based on a self-assembled monolayer field-effect transistor (SAMFET) was used to detect the biomarker nitric oxide. A SAMFET based sensor is highly sensitive because the analyte and the active channel are separated by only one monolayer. SAMFETs were functionalized for direct NO detection using iron porphyrin as a specific receptor. A threshold voltage shift towards positive gate biases with increasing NO content was observed. The sensor response was examined as a function of NO concentration. High sensitivity has been demonstrated by detection of ppb concentrations of NO. Preliminary measurements have been performed to determine the selectivity.

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6.1 Introduction

Human noses can perceive hundreds of thousands of different odor molecules.[1] The olfactory system consists of an array of receptors, each of which detects a limited number of substances. This complex system warns about dangers such as fire, air pollutants or spoiled food. In the past decades electronic noses have been developed that mimic the human olfactory system.[2] An electronic nose comprises a gas sampling unit and an array of chemical sensors. Various transducers can be used like carbon black or conducting polymer based chemiresistors, metal oxide semiconductor field-effect transistors, and surface or bulk acoustic wave resonators.[3] The sensors themselves are not selective; a fingerprint of the smell is obtained and a neural network is incorporated for pattern recognition.

An emerging application is the detection of the biomarker nitric oxide (NO). NO plays an important role in biological functions by acting as a neurotransmitter and by regulating the relaxation of blood vessels.[4] Furthermore NO is a marker for airway inflammations such as asthma.[5] Measurement of the NO concentration in exhaled breath is applied to diagnose and monitor the inflammation and the obtained information is used as a tool to manage the asthma treatment. NO detection is based on electrochemical, optical or electrical techniques.[6,7] Typically, NO is detected indirectly since NO is first converted into NO_2 by *e.g.* CrO_3 or ozone.[8] Although NO sensors are commercially available,[9] there is a demand for small, sensitive NO transducers for point of care use.[10,11]

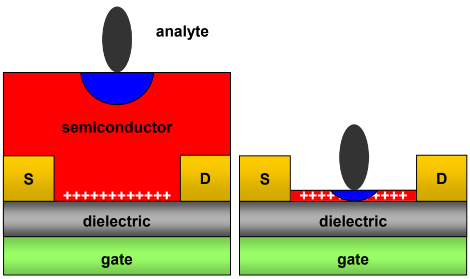

Figure 6.1: Schematic representation of the operation principle of a SAMFET sensor. The transistor consist of an organic semiconductor, a source and drain electrode, a gate dielectric and a gate. A conducting channel is formed at the semiconductor gate dielectric interface. On the left side, analyte molecules are absorbed on top of a thick semiconductor layer. The current modulation is limited by the thickness of the semiconductor. The electrostatic interactions are stronger when the distance between the analyte and the channel is decreased. Hence a monolayer thick semiconductor (right) yields the ultimate sensing performance.

6.2 Self-assembled monolayer field-effect transistor

Here a new sensitive gas sensor based on self-assembled monolayer field-effect transistors (SAMFET) is introduced. The proof-of-principle is demonstrated by direct detection of NO. The operation principle is elucidated in figure 6.1. The left side shows a standard organic field-effect transistor consisting from top to bottom of an organic semiconductor, a source and drain electrode, a gate dielectric and a gate. Upon applying a bias to the gate, charge carriers are accumulated at the gate dielectric-semiconductor interface. A conducting channel is formed with a thickness of approximately 1 - 2 nm.[12] Analyte molecules absorbed on top of the semiconductor can modulate the charge transport in the channel by electrostatic interactions. However, it has been demonstrated by Huang *et al.*[13] that the sensitivity of such a sensor is dependent on the thickness of the active layer. The response of organic transistors to nerve agent simulants increased dramatically with decreasing layer thickness, due to the strong distance dependence of the electrostatic interactions. Torsi *et al.*[14] have reported chiral sensors and argue that the sensing is restricted to the conducting channel. The sensitivity did not increase with decreasing layer thickness but this could be due to the granular nature of the semiconducting films. Finally, sensitivity enhancement of up to an order of magnitude has been reported in transistors by using ultra thin semiconducting films.[15] Hence a semiconductor of only one monolayer thickness should yield the most sensitive gas sensor, as shown in figure 6.1 on the right.

A SAMFET has recently been reported by Smits et al.[16] The monolayer consists of molecules with a semiconducting quinquethiophene core and an aliphatic spacer that is attached to the gate dielectric with a monofunctional anchoring group. The chemical structure of chloro[11-(5''''-ethyl-2,2':5',2'':5'',2''':5''',2''''-quinquethien-5-yl)undecyl] dimethylsilane is shown in the inset of figure 6.2. The SAMFETs were fabricated on heavily doped *n*-type Si wafers, acting as common gate electrode, with a 1000 nm thermally oxidized SiO_2 layer as gate dielectric. Au source and drain electrodes were defined by conventional photolithographic methods, resulting in ring transistors with a channel length of 10 μm and a width of 2500 μm. Semiconducting monolayers were self-assembled from a toluene solution on a HF activated SiO_2 dielectric, as described in the previous chapter. The SAMFETs were annealed in vacuum at 110 $^\circ$C for one hour to remove residual water and solvents. Electrical measurements were performed under vacuum using an HP 4155B semiconductor parameter analyzer. Possible gate bias stress effects in the electrical measurements were prevented by using a short integration time of less than 1 ms per step. A typical transfer curve is presented in figure 6.2. The mobility is about 0.01 cm^2/Vs and the current modulation 6 decades, in good agreement with previous

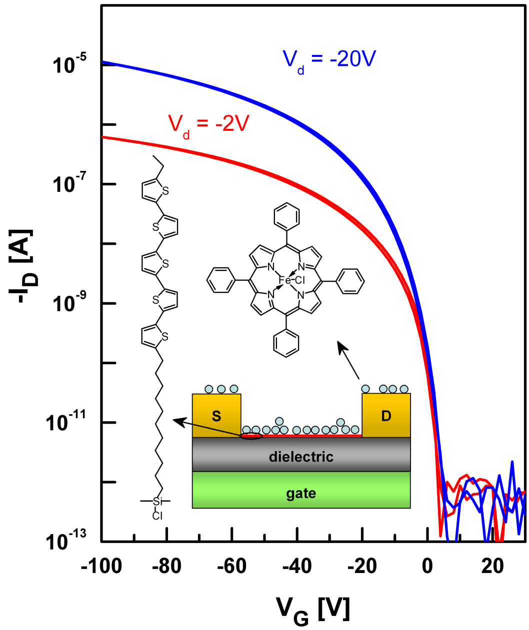

Figure 6.2: Transfer characteristics of a typical SAMFET in vacuum with a 1 μm SiO_2 gate dielectric in the linear and saturated regime. The device exhibited *p*-type behavior with a pinch off voltage around 0 V. The inset shows a schematic cross-section of the SAMFET sensor. The chemical structures of the SAM molecule (left) and the NO receptor Fe(TPP)Cl (above) are shown.

reports.

6.3 Results and discussion

The response of the SAMFETs was measured by admitting small amounts of NO, diluted in nitrogen carrier gas, to the closed chamber. The gas pressure in this static system was used to calculate the partial NO concentration at 1 bar. The response of the SAMFET itself to NO is indistinguishable from random drift of the threshold voltage. To make the SAMFET specific for NO, a porphyrin receptor was used. Porphyrins are known to bind NO in *e.g.* biological systems.[17] Here iron(III) tetraphenylporphyrin chloride (Fe(TPP)Cl, Sigma Aldrich) was applied, that was previously used to detect NO in solution with a molecular controlled semiconductor resistor.[18] In the ideal case this receptor is grafted on, or incorporated into, the monolayer. Here, to demonstrate the concept, a thin spin coated film was used. The porphyrin receptor was dissolved in toluene, 1.6 mg/ml, and thin layers were spincoated at 800 rpm. The films are only 10 nm thick and they contain a lot of pinholes. Therefore the diffusion of the nitric oxide is not limiting the detection rate. The addition of porphyrin on the SAMFET had no significant influence on the performance of the SAMFET. The chemical structure and the device lay-out are schematically depicted in the inset of figure 6.2. The transfer curve of the SAMFET with the porphyrin shifts upon exposure to NO. The field-effect mobility remains unaffected; the only effect is a change in the threshold voltage towards positive gate bias. This clearly points to an increase of fixed negative interface charges upon exposure to NO. However, the reaction is not instantaneous, the threshold voltage shifts with time. A typical example is presented in figure 6.3. A possible reason might be the slow supply of negatively charged minority carriers needed to convert NO into NO_x^-, an effect that is presently under study. The threshold voltage shift takes about half an hour to saturate. Hence, in order to arrive at a dose response curve, the transfer curves were measured 30 minutes after NO exposure. To exclude any influence of competing charging effects, the threshold voltage of the SAMFET was monitored in the absence of NO. This measurement did not reveal a change of threshold voltage in time. The response to NO of the SAMFET without porphyrin was also investigated. These reference measurements are shown in figure 6.3. Only the combination of the SAMFET and the receptor in NO atmosphere yields a shift in threshold voltage.

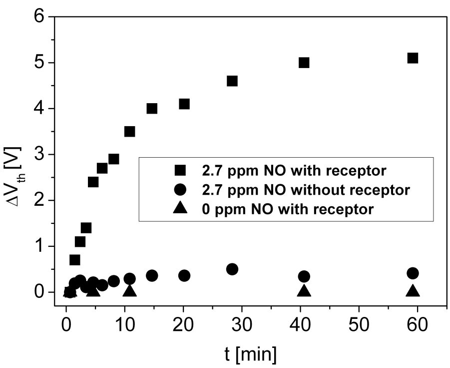

Figure 6.3: The response of the SAMFET sensor as a function of time for a fixed NO concentration (2.7 ppm). The threshold voltage shifts towards more positive voltages and saturates after approximately 30 minutes. Reference measurements of the SAMFET without the porphyrin in NO (2.7 ppm) and the SAMFET with porphyrin in absence of NO are included. Only the combination of the SAMFET and the receptor in NO shows a threshold voltage shift that stands out over random drift.

Many sensors were made and their response to NO was investigated. Figure 6.3

discussed above showed a typical measurement for 2.7 ppm NO. Concentrations in the ppm regime can reproducibly be detected. In exceptional cases however a much higher sensitivity has been measured. An example is presented in figure 6.4 where the transfer curves measured in the linear regime are presented on a linear scale as a function of the NO concentration. The transfer curve systematically shifts to positive gate biases with increasing NO content. The relative threshold voltage shift, V_{th}, was determined by taking the gate biases yielding a fixed source drain current of 60 nA, as indicated by the arrow in figure 6.4. The shifts are used to construct a dose response curve. The inset shows the threshold voltage shift as a function of the NO concentration. The dose response curve shows that with the SAMFET sensor ppb concentrations of NO can be detected. The achieved sensitivity compares favorably with an earlier reported detection limit of an NO sensor based on a field-effect transistor.[19]

The magnitude of the shift and the functional dependence such as the apparent saturation at high NO content are not yet quantitatively understood. Various operation mechanisms have been reported. For instance Fe(TPP)Cl has been attached to functionalised GaAs surfaces.[18] The current was measured upon exposure to NO in aqueous buffer solution. The current did increase with NO content. The change in current was explained as originating from a change in dipole moment of the Fe(TPP)Cl complex. However a threshold voltage shift in a field-effect transistor cannot be explained with only a change in surface dipole moment.[20] A different reaction mechanism was proposed by Lin and Farmer.[21] In solution NO forms a complex with Fe(TPP), NO-Fe(TPP). Catalytic reaction of this nitrosyl-complex with free NO then yields amongst others NO_2 which is known to cause a shift in threshold voltage[22] presumably by formation of negative surface charges. Recently, ZnO chemiresistors have been functionalised with a comparable iron(III)porphyrin, viz. ferriprotoporphyrin IX chloride.[23] NO could be detected down to the ppm range. The operation is reported to be due to electron transfer from ZnO to the receptor. In summary, iron porphyrins could selectively react towards NO, but the microscopic mechanism is unknown.

The selectivity of the SAMFET sensor versus other vapors was investigated. Preliminary experiments show that the sensor is not sensitive to a variety of gases. No threshold voltage shift was observed for non oxidizing agents as toluene (8 ppm), methanol (%) and ammonia (2 ppm). Even for oxidizing agents as O_2 and SO_2 the threshold voltage shift is negligible showing the selectivity of the porphyrin towards these gases. Reversibility of the sensor after NO detection was also examined. Full recovery of the sensor is achieved by annealing under vacuum condition at 110 °C for 1 hour. Under those conditions the threshold voltage returns to its pristine value. Our explanation is that the threshold voltage shift upon NO exposure is due to the formation of NO_x^-. At elevated temperature the

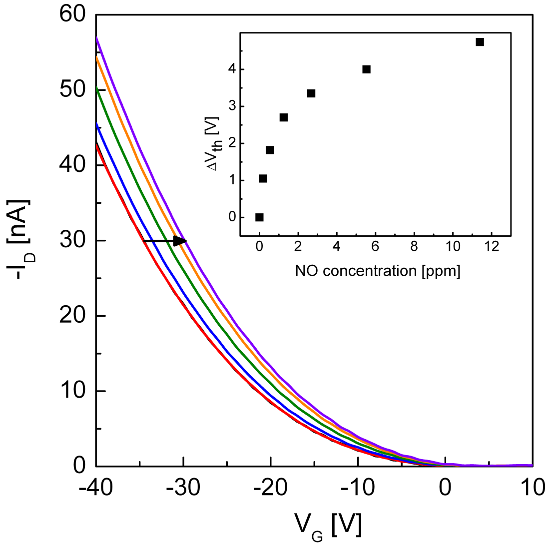

Figure 6.4: Linear plot of the transfer characteristics of the SAMFET sensor. The measurements performed in vacuum and nitrogen were identical. The transfer curve measured 30 minutes after exposure is shifted towards positive values for increasing NO concentrations. The inset shows the threshold voltage shift as a function of NO concentration. The detection limit is as low as sub 100 ppb NO.

equilibrium shifts to neutral nitrogen oxides that subsequently desorb from the surface. This could explain the full reversibility. A major problem still to be resolved is that a significant spread in the NO response was found for the numerous investigated SAMFET sensors. The differences can be due to imperfections in the monolayer, variations in the porphyrin converter deposition, or parasitic reactions with residual water. The latter becomes more important at lower NO content.

6.4 Conclusion

The response of a field-effect sensor is dominated by the electrostatic interactions between analyte and the conducting channel. In a self-assembled monolayer field-effect transistor the semiconductor is only one molecule thick, making it highly suited for sensing applications. SAMFET sensors were fabricated using iron porphyrin as a specific receptor for the biomarker NO. The transfer curve systematically shifts to positive gate biases with increasing NO content. Dose response curves were obtained by plotting the threshold voltage shift as a function of NO concentration. High sensitivity was demonstrated by detecting parts per billion concentrations NO.

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